EUBCE 2016
AMSTERDAM
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Influence of feedstock demineralization on the chemical composition of pyrolysis vapours derived from sugarcane residues in py-GC/MS

June, 08th 2016, 24th European Biomass Conference

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UDT

Lignocellulosic materials obtained from sugarcane processing

Mechanical harvesting (75%)

Leaves and cane tops

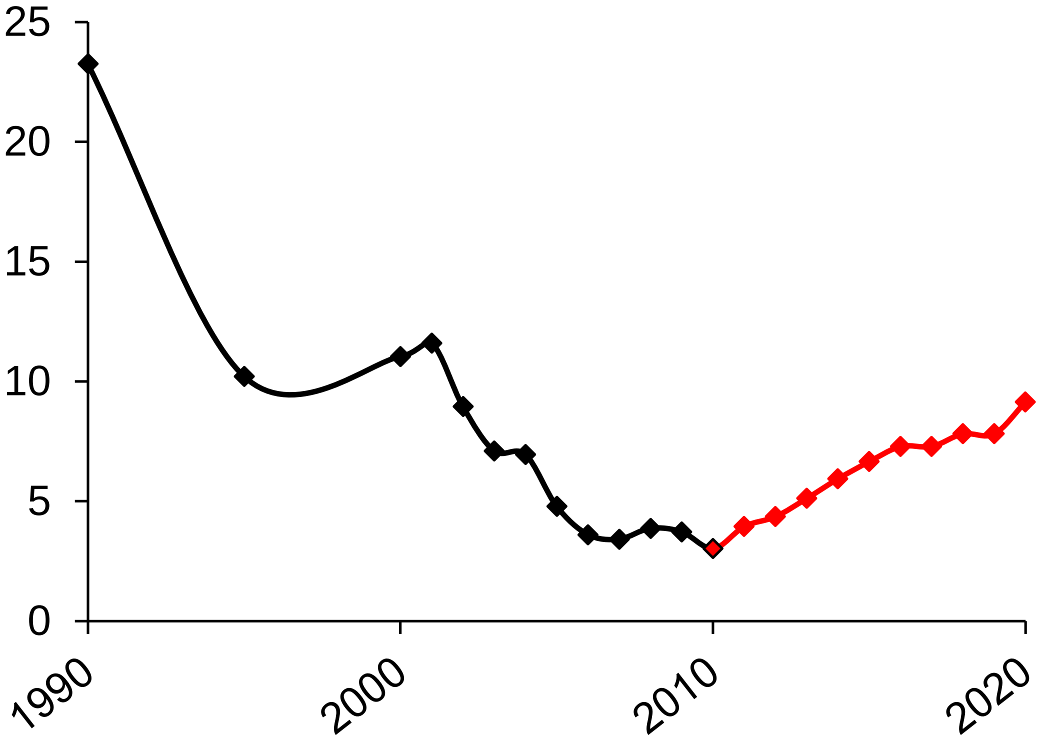
Sugarcane trash (SCT)

Extraction of the juice

Plant stalk

Sugarcane bagasse (SCB)

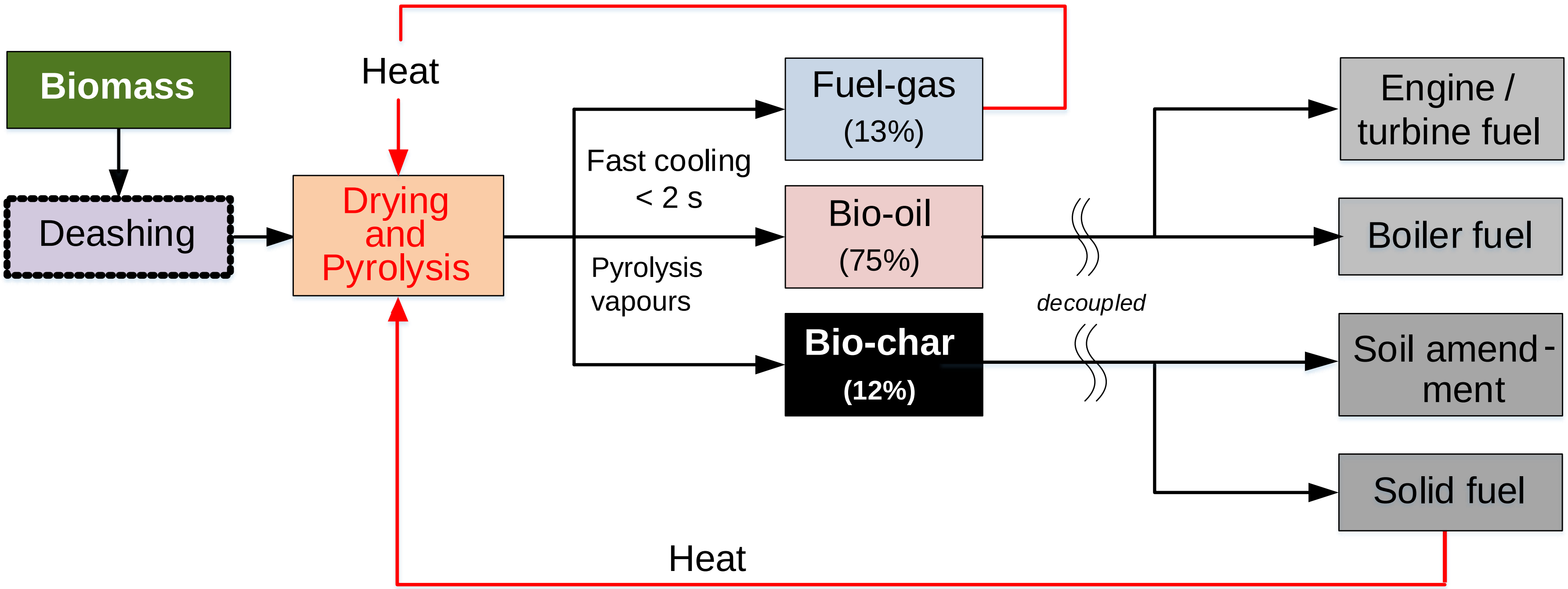
Production of sugarcane bagasse in Cuba (Mton)



Statistical Yearbook of Cuba, **2015**

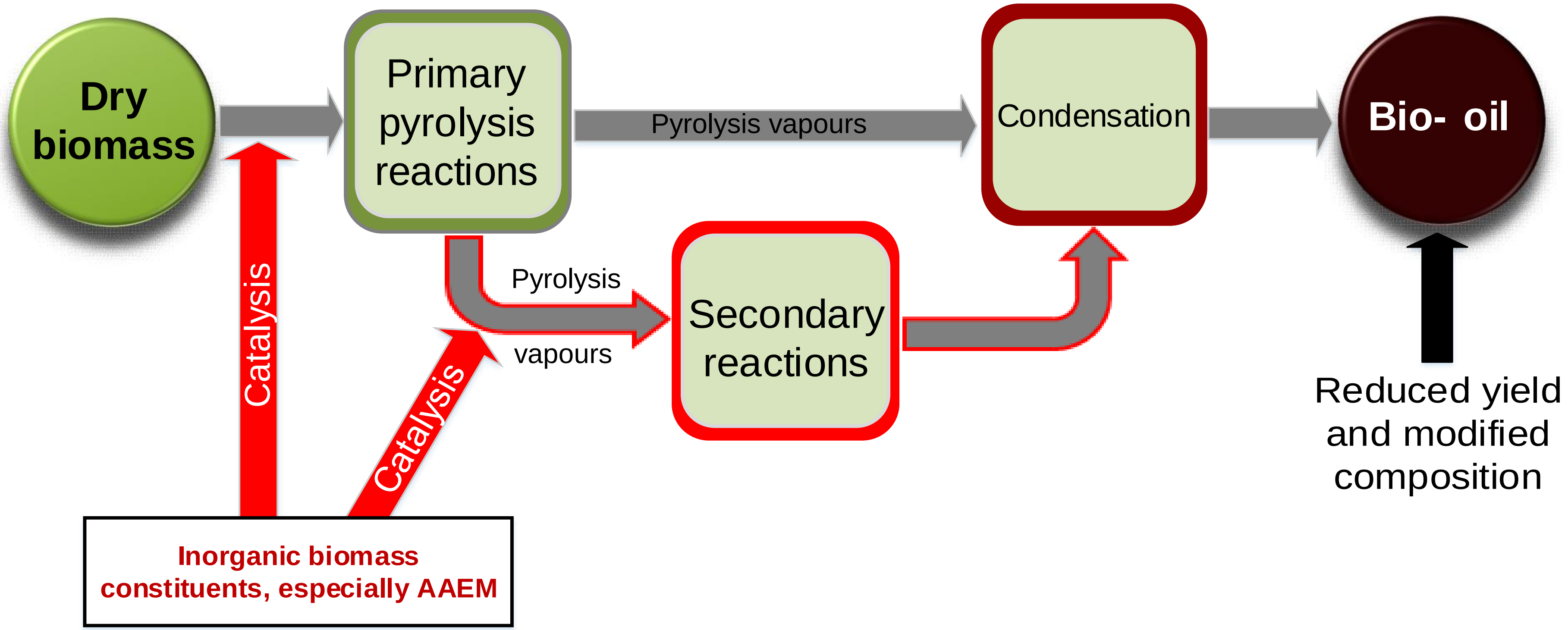
Sugarcane biomass residues	Availability, ton/ton crushed cane (Use)	Surplus available
Bagasse + trash in sugar mill	**0.32** (Steam supply and power generation)	**15-20%**
Trash left in field	**0.17** (Improve soil quality)	**?**
Trash separated in cane cleaning centers	**0.11** (Power generation)	**40%**

Fast pyrolysis fast platform for sugarcane lignocellulosic residues



Rodriguez et al., **1987.** Sugar cane bagasse as a feedstock for an industrial fast pyrolysis process under development. Journal of Analytical and Applied Pyrolysis, 12, 301-318

Influence of inorganic biomass constituents on pyrolysis results



Eom et al. **2012**. Effect of essential inorganic metals on primary thermal degradation of lignocellulosic biomass. Bioresource Technology, 104(0), 687-694.

General objective: to evaluate the effect of demineralization of sugarcane bagasse and sugarcane trash on the chemical composition of the bio-oil, viz. by applying micro-pyrolysis (py-GC/MS).

Feedstock preparation prior to leaching

SCT

SCB

Preparation of original biomass samples

Drying
- Ambient atmosphere during 3 days

Grinding
- 1 kg in a small cutter mill

Classifying
- 0.45 kg particle size range 1-2 mm

SCT: sugarcane trash
SCB: sugarcane bagasse

Characterization of untreated samples

Proximate analysis, wt.%			Ultimate analysis, wt.% d.b.			ICP-OES analysis, mg/kg		
	SCB	SCT		SCB	SCT		SCB	SCT
Volatile matter[d.b.]	79.8	73.9	C	44.1	40.1	K	1,800	2,300
Fixed carbon[a]	17.1	19.2	H	6.0	5.3	Na	32.1	56.8
Moisture[a.r.]	6.7	7.1	O[a]	47.7	48.8	Mg	287	492
Ash[d.b.]	**1.8**	**5.3**	N	0.2	0.5	Fe	327	245
						Al	279	216
						Si	8,600	13,400

Ash of pine wood: 0.33 wt.% d.b.

[d.b.] On dry basis
[a] Calculated by difference
[a.r.] As received basis
Sulphur: below detection limit

Leaching conditions

SCT

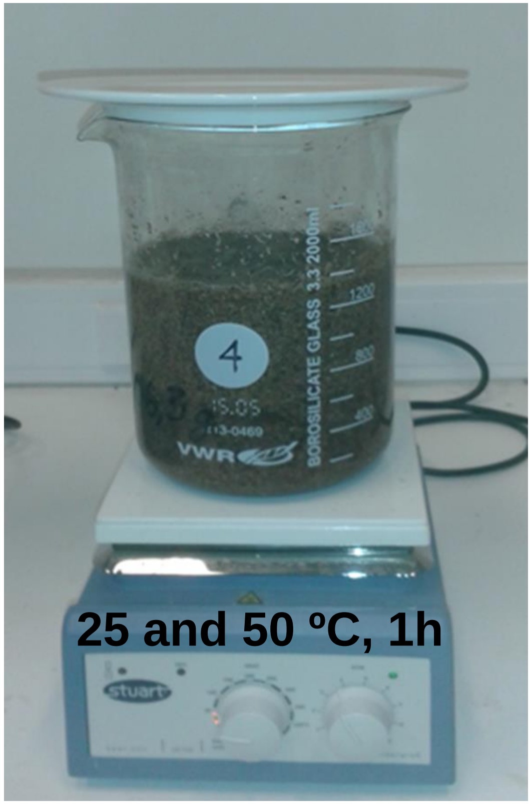
SCB

Water (W)

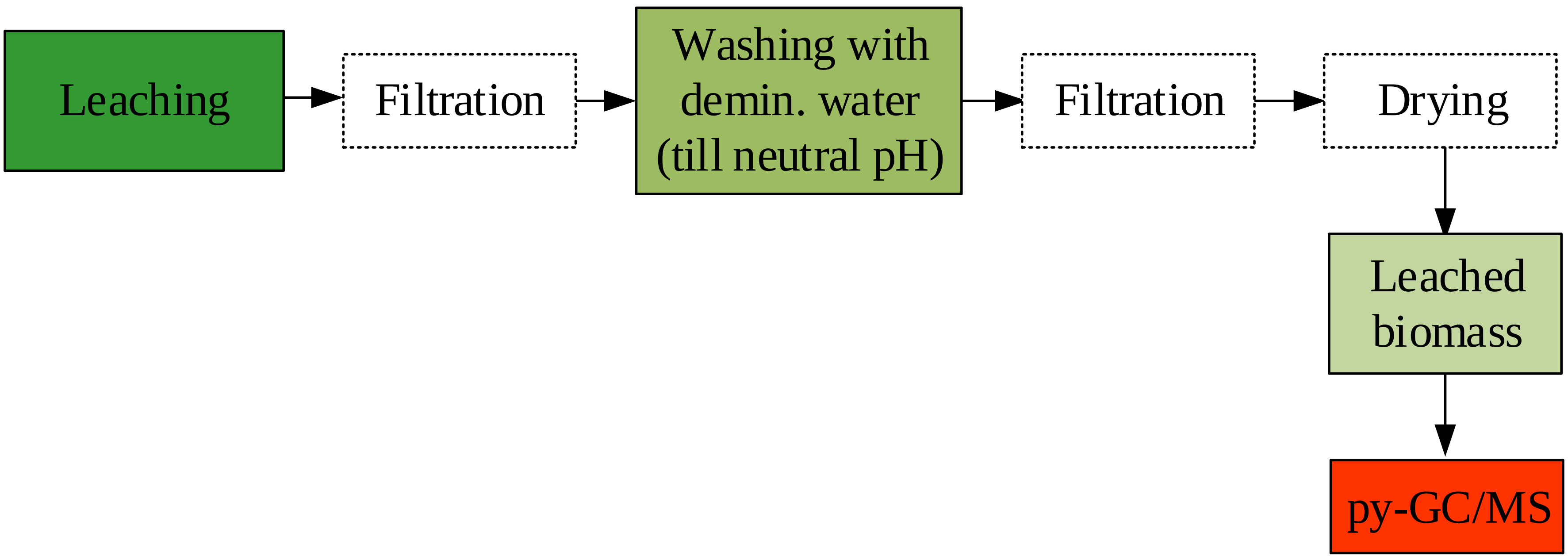
HCl, (5M)

H_2SO_4, (5M)

Citric acid (CA), (1M)



Biomass processing



Proximate (*wt.*%) and ICP-OES analysis (mg/kg) of biomass leached at 25 ºC, 1h

Washing agent	SCB					SCT				
	Unt.	Water	HCl	CA	H_2SO_4	Unt.	Water	HCl	CA	H_2SO_4
V.M.[d.b.]	**79.8**	82.3	80.7	80.7	79.8	**73.9**	77.4	76.1	76.9	76.7
F.C.[a]	**17.1**	17.1	17.6	17.6	18.6	**19.2**	17.8	19.4	18.4	19.1
Moisture[a.r.]	**6.7**	3.1	3.0	3.4	2.8	**7.1**	3.4	3.9	5.0	3.2
Ash[d.b.]	**1.8**	1.3	1.1	1.1	1.1	**5.3**	4.2	3.6	3.7	3.6
A.R. (%)	**-**	33.6	48.4	48.4	48.4	**-**	29.4	47.4	38.9	45.6
K	**1,800**	293.0	17.5	17.0	15.7	**2,300**	142.0	16.2	17.6	13.2
Na	**32.1**	15.8	18.6	<5.0	8.02	**56.8**	6.14	49.2	< 5.0	24.3
Mg	**287**	198.0	25.1	68.1	26.4	**492**	330.0	14.1	29.6	19.9
Fe	**327**	209.0	110.0	123.0	101.0	**245**	122.0	61.5	104.6	73.3
Al	**279**	180.0	110.0	131.0	122.0	**216**	101.0	54.0	78.0	59.8
Si	**8,600**	4,500	3,600	4,400	4,400	**13,400**	15,600	14,600	6,300	11,000

V.M. Volatile matter
F.C. Fixed carbón
A.R. Ash removal
Unt. Untreated

[d.b.] On dry basis
[a] Calculated by difference
[a.r.] As received basis
Sulphur: below detection limit

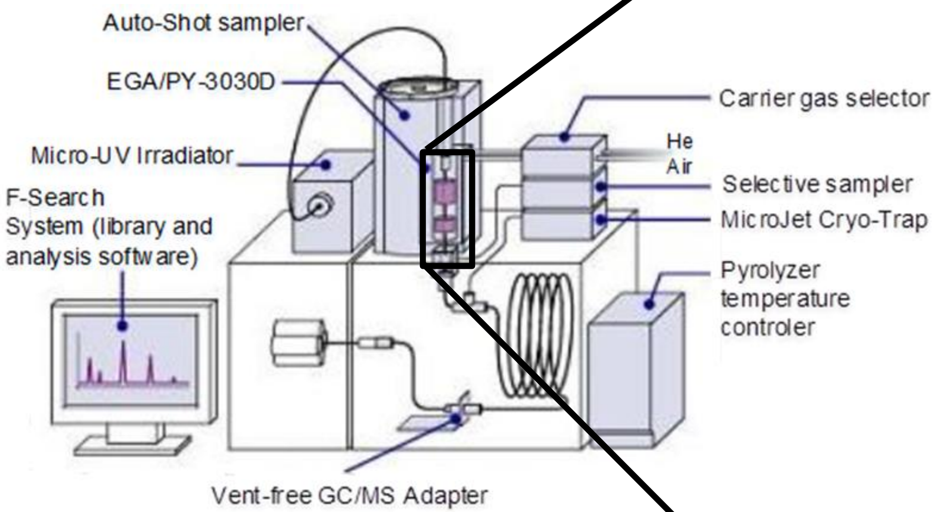
Proximate (*wt.*%) and ICP-OES analysis (mg/kg) of biomass leached at 50 ºC, 1h

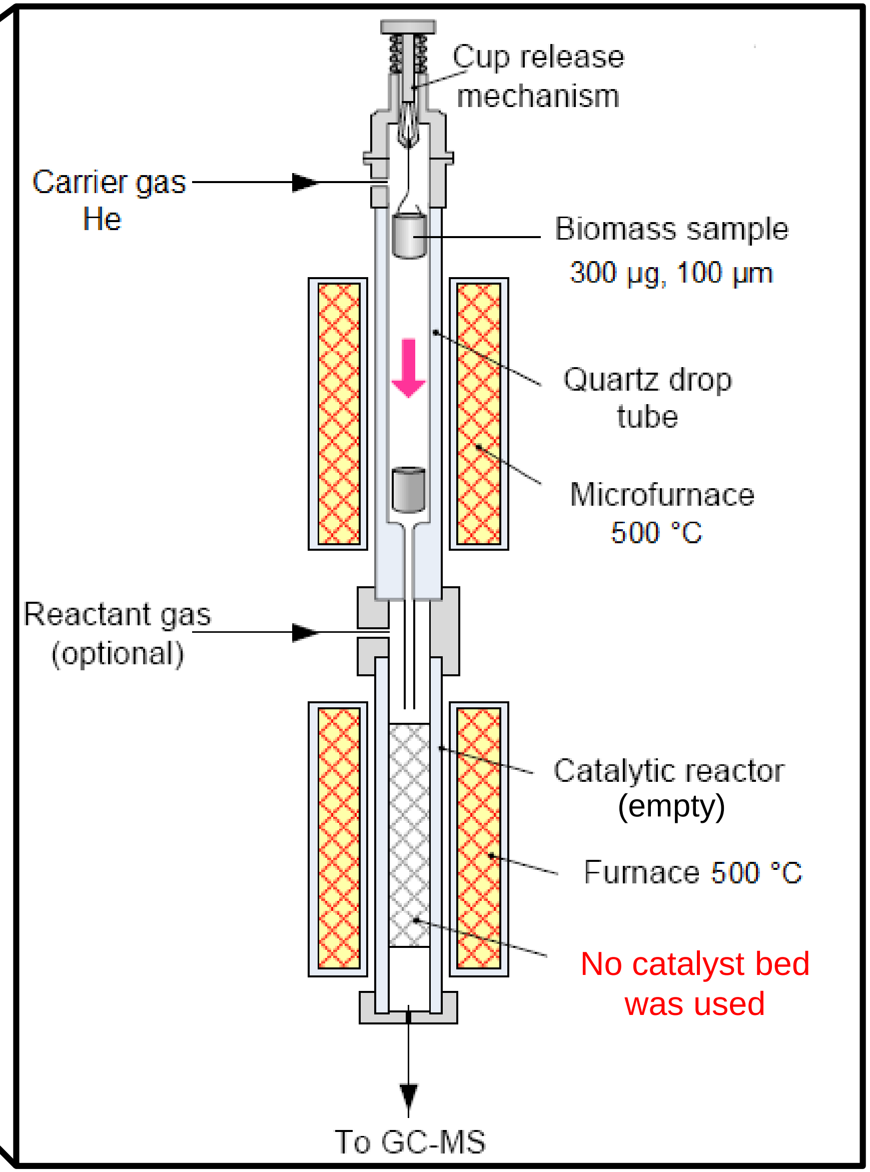
Washing agent	SCB					SCT				
	Unt.	Water	HCl	CA	H_2SO_4	Unt.	Water	HCl	CA	H_2SO_4
V.M.[d.b.]	**79.8**	81.6	80.0	80.5	73.9	**73.9**	76.8	74.3	75.4	70.9
F.C.[a]	**17.1**	16.3	18.1	17.7	24.1	**19.2**	18.3	20.1	18.7	23.2
Moisture[a.r.]	**6.7**	4.3	2.4	3.8	2.0	**7.1**	2.9	3.1	5.2	3.1
Ash[d.b.]	**1.8**	1.4	1.4	1.0	2.4	**5.3**	4.4	5.1	3.8	5.2
A.R. (%)	**-**	31.1	48.2	50.1	54.7	**-**	26.9	45.2	39.0	46.6
K	**1,800**	125.0	26.9	11.2	11.8	**2,300**	219.0	16.7	12.3	15.2
Na	**32.1**	16.0	21.5	4.8	5.3	**56.8**	15.1	46.7	< 5.0	<5.0
Mg	**287**	143.0	18.8	25.2	15.3	**492**	256.0	9.4	56.9	28.4
Fe	**327**	138.0	74.5	68.7	52.5	**245**	113.0	73.7	80.0	89.9
Al	**279**	119.0	138.0	65.0	103.3	**216**	206.6	62.7	55.1	158.3
Si	**8,600**	3,275	3,700	2,916	3,956	**13,400**	15,600	13,700	<200.0	19,110

V.M. Volatile matter
F.C. Fixed carbón
A.R. Ash removal
Unt. Untreated

[d.b.] On dry basis
[a] Calculated by difference
[a.r.] As received basis
Sulphur: below detection limit

Micro-pyrolysis setup





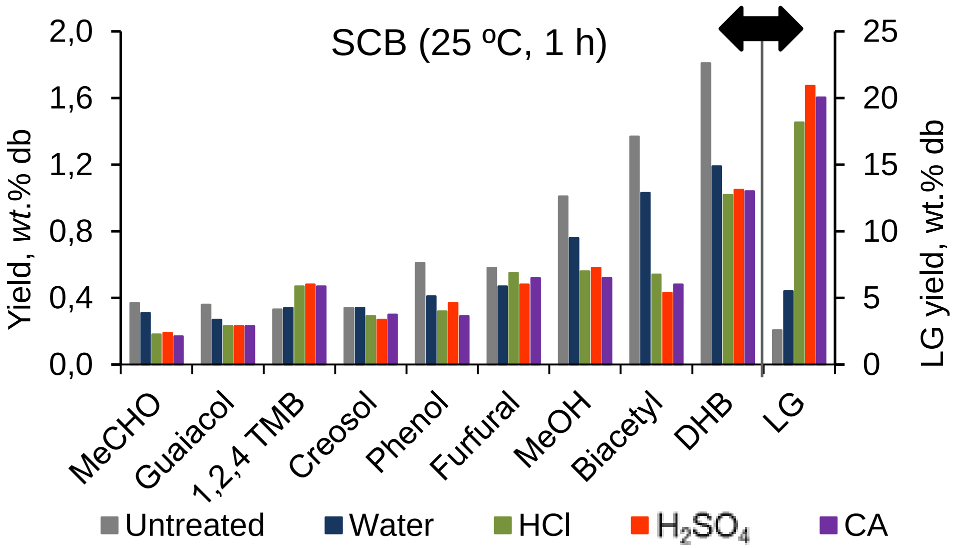
Frontier Laboratories. Multi-Shot Pyrolyzer, EGA/PY-3030D. www.frontier-lab.com, 2016

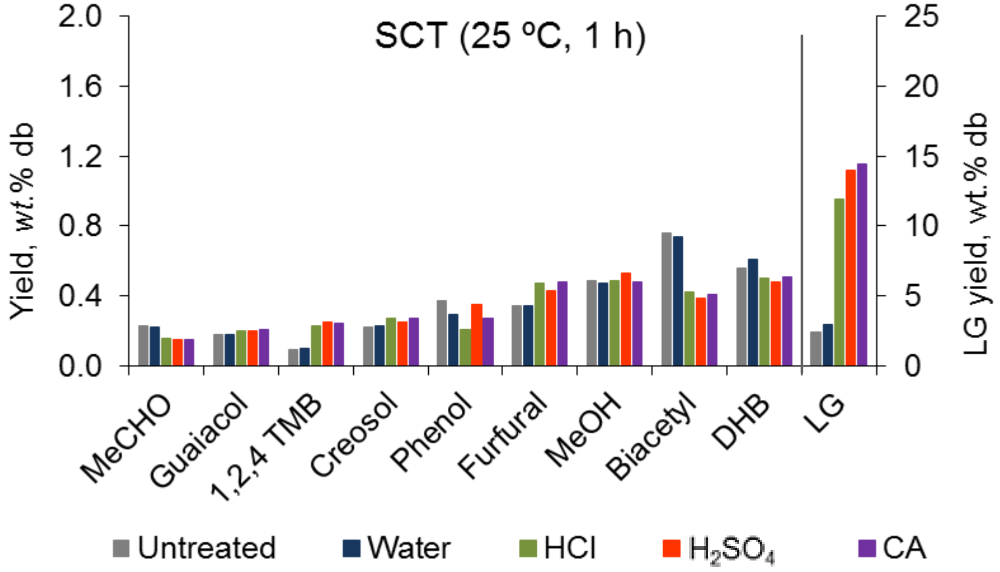
Calibrated vapour phase compounds

Compound name (Trivial name or abrev.)	Formula	Origin[a]
Acetaldehyde (MeCHO)	C_2H_4O	C
Methanol (MeOH)	CH_4O	C/L
2,3-Butanedione (Biacetyl)	$C_4H_6O_2$	C
2-Furaldehyde (Furfural)	$C_5H_4O_2$	C
Phenol	C_6H_6O	L-H
2-Methoxyphenol (Guaiacol)	$C_7H_8O_2$	L-G
2-Methoxy-4-methylphenol (Creosol)	$C_8H_{10}O_2$	L-G
2,3-dihydrobenzofuran (DHB)	C_8H_8O	Un.
1,2,4-trimethoxybenzene (1,2,4TMB)	$C_9H_{12}O_3$	Un.
1,6-anhydro-β-D-Glucopyranose, Levoglucosan (LG)	$C_6H_{10}O_5$	C

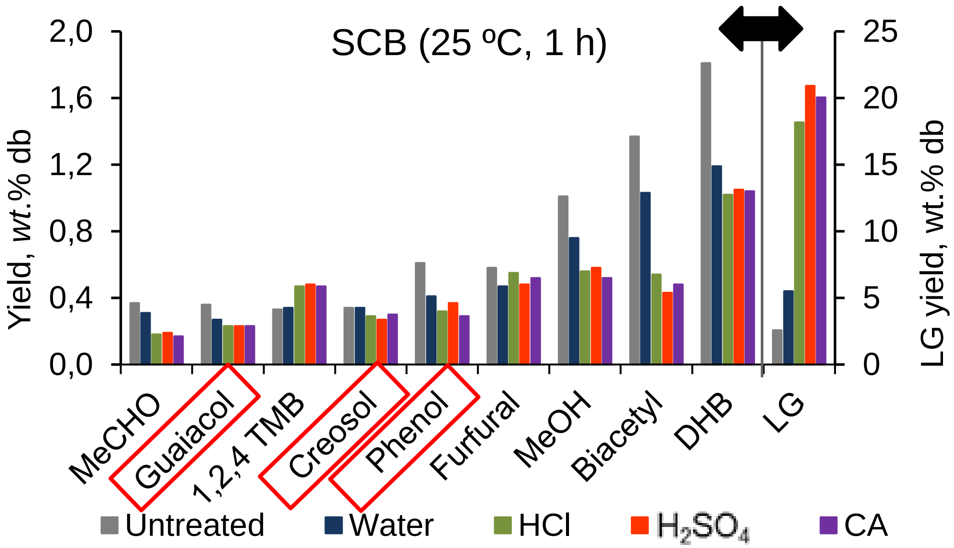
[a] C, L, L-H, L-G, Un. represent cellulose, lignin, p-hydroxyphenyl lignin, guaiacyl lignin and unknown, respectively.

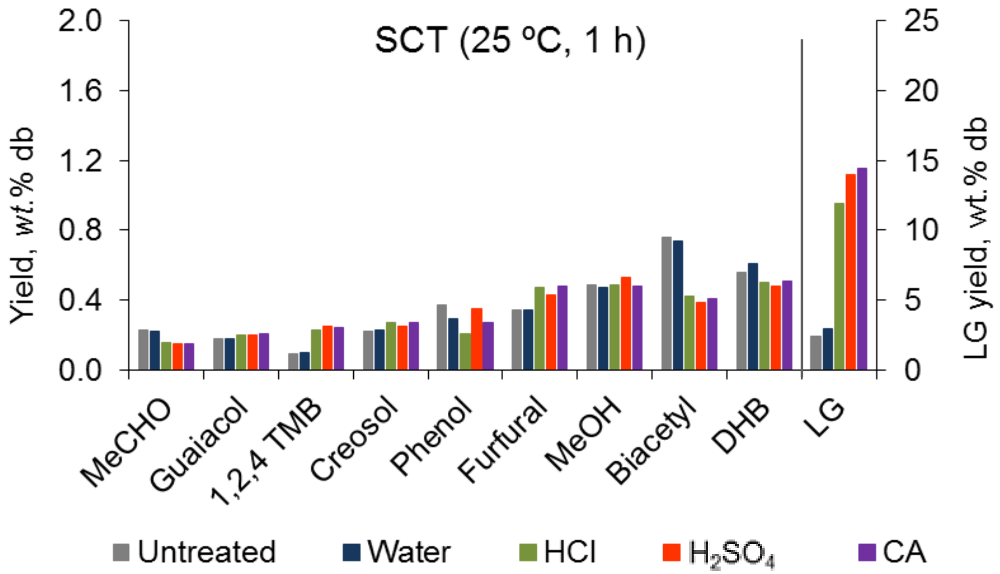
Yield of calibrated vapour phase compounds of leached biomass (*wt*.% on d.b.)



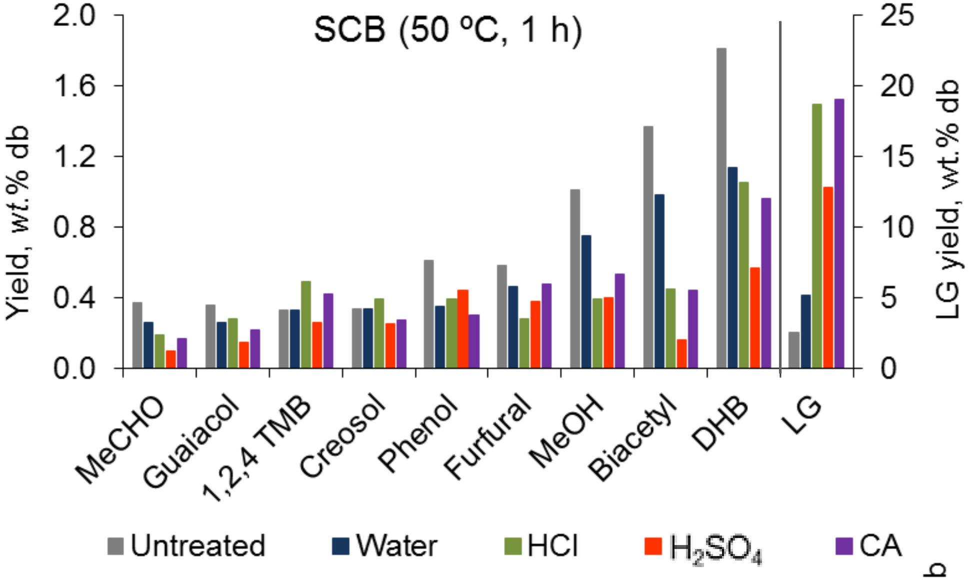


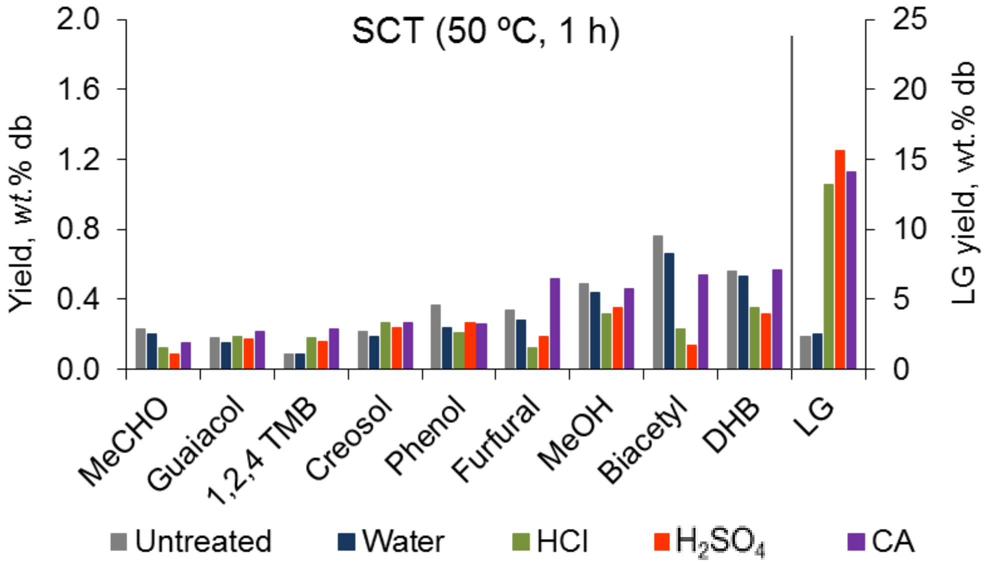
Yield of calibrated vapour phase compounds of leached biomass (*wt*.% on d.b.)





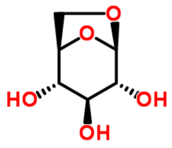
Yield of calibrated vapour phase compounds of leached biomass (*wt*.% on d.b.)





Effect of acid leaching

Levoglucosan ⬆



- Decreasing in AAEM = decreased catalysis
- Decreasing of cellulose crystallinity ?
- Prehydrolysis ?

Conclusions

- The results of this work suggest that chemical treatment of SCB and SCT, either with inorganic (HCl, H_2SO_4) or organic (CA) acids, increases the yields of levoglucosan in their volatiles between 10-18 (SCB) and 9-13 (SCT) *wt.*%.

- SCT also is a valuable feedstock for fast pyrolysis as its spectrum of pyrolysis vapour compounds is similar to that of SCB.

- Citric acid could be considered as a leaching solution.

- The volatile compounds distribution of citric acid treated biomass showed small variations upon changing the pretreatment temperature.

- The yield of lignin-derived compounds decreases slightly when sugarcane biomass is treated.

Support from: BOF and Project FONDECYT 11150148.

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